

ELECTRODEPOSITION OF PALLADIUM-NICKEL ALLOY

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[Received: 1989 November; Accepted: 1990 May]

It is well known that palladium-nickel alloy can help considerably in bringing down the consumption of gold in the electronics industry. The silvery white appearance of the alloy makes it a good alternative to rhodium plated jewellery and other decorative applications also. This paper describes a suitable method for depositing the alloy and some of its properties.

Key words: Electrodeposition, Pd-Ni alloy, ammine chloride electrolyte

INTRODUCTION

The escalation in the price of gold has necessitated the use of a viable substitute for it in the jewellery trade as well as in the electronics industry [1-3]. Though electrodeposited palladium can replace gold in certain electronic applications, it is said to possess some inherent disadvantages, namely dull appearance, high porosity, low ductility and tendency to film formation, especially in the presence of organic vapours and in sulphur containing atmospheres on storage, leading to an increase in the contact resistance of the deposits [4]. An alloy of palladium and nickel, already known to obviate these disadvantages is finding increasing applications in the electronics industry [5] as in the case of jewellery, for decorative plating. This paper describes the deposition of palladium-nickel alloy from an ammine chloride electrolyte and the studies relating to deposition characteristics of the electrolyte.

EXPERIMENTAL

Palladium was taken in the form of its ammine chloride complex, prepared from palladium chloride using standard procedures available in the literature [6]. This complex was used with a slight excess of ammonia. Ammonium chloride was added as the buffer and a conducting salt. Nickel was introduced in this solution as its sulphate salt. The pH of the electrolyte was adjusted to 8.5 with ammonia electrometrically. Platinum in the form of a foil or platinised titanium was employed as the insoluble anode and its area was maintained 2 to 3 times that of the cathode in order to minimise excessive anode polarisation which results in lowering of pH at the anode and subsequent precipitation of the palladium diammine complex. The bath composition used was as follows:

Palladium as its complex	— 0.17 - 0.2M
Nickel as its sulphate	— 0.25 - 0.3M
Ammonium chloride	— 0.15 - 0.2M
pH	— 8.5

Deposits prepared on platinum cathode were stripped in 1:1 (V/V) hydrochloric acid and estimated for nickel colorimetrically. For other tests, deposits were produced on copper or nickel plated copper substrates. The partial cathode efficiencies were calculated using the conventional method [7].

Tests were also performed using a 267 ml Hull cell with a cell current of 1A for 5 minutes. The panels were initially electroplated with nickel to a thickness of 5.0 μm prior to alloy deposition. Experiments were conducted in presence of certain additives also.

The throwing power of the electrolyte was measured using a Haring and Blum cell [8], with a current distribution ratio of 5. The Field's formula [8] was used to calculate the metal distribution efficiency of the electrolyte.

The reflectivity of the dull and bright deposits was measured by means of a Gloss meter with a vacuum coated silver mirror as the standard. The deposits were examined for their smoothness with a Perthometer at a thickness level of 5.0 μm and their percentage levelling assessed.

The hydrogen permeation in the alloy deposits was measured by the method of Devanathan et al [9]. Values of maximum permeation current, residual permeation current and quantity of adsorbed hydrogen were calculated [10] from the plots of permeation currents at various time intervals for a total duration of upto 900 seconds.

RESULTS AND DISCUSSION

Table I shows the effect of operating variables on the nickel contents and appearance of alloy deposits. The nickel content of the alloy was found to increase with the Ni/Pd ratio in solution and deposits corresponding to ratios of 1.0 - 1.5 had silvery white appearance. Conditions conducive to production of silvery white, smooth deposits and with considerable nickel contents were: a current density of 10-20 $\text{mA}\cdot\text{cm}^{-2}$, pH of 8.5 - 9.5, room temperature and with the solution being

unstirred. Deposits obtained at current densities below 10 mA.cm^{-2} , at higher temperatures and with solution agitation were gray black in appearance.

TABLE-I: Effect of operating conditions on the nickel contents and appearance of alloy deposits

Sl. No.	Ni/Pd ratio	C.d. (mA.cm^{-2})	pH	Temperature (K)	Ni content (%)	Nature of deposit
1.	0.15	10	8.5	303 ± 2	8.0	Grey matte
2.	0.5	10	8.5	302	12.5	Semi bright
3.	1.0	10	8.5	302	16.0	Semi bright
4.	1.25	10	8.5	302	20.0	Semi bright
5.	1.5	10	8.5	302	24.0	Matt
6.	2.0	10	8.5	302	33.0	Grey matte
7.	1.25	5	8.5	302	22.0	Grey black
8.	1.25	5*	8.5	302	35.0	Black
9.	1.25	15	8.5	302	19.0	Semi bright
10.	1.25	15*	8.5	302	22.0	Black
11.	1.25	20	8.5	302	15.0	Semi bright
12.	1.25	20*	8.5	302	18.0	Grey matt
13.	1.25	30	8.5	302	10.0	Powdery
14.	1.25	10	7.5	302	25.0	Grey matt
15.	1.25	10	9.5	302	17.0	White smooth
16.	1.25	10	8.5	317	22.0	Grey
17.	1.25	10	8.5	327	24.0	Black

* With stirring

Figure 1 also shows the partial cathode efficiencies for nickel and palladium deposition. It is observed that the gray black deposits result, whenever, the hydrogen evolution is substantial [11]. This indicates that palladium in the alloy is in the β phase in which the solubility of hydrogen is very high (3-57 atomic percent) [12]. Levels of pH higher than 9.0, though helpful for production of smooth, white deposits, operating the bath at a pH of 8.5 is to be preferred due to the lower nickel content of the alloy and to the difficulty in maintaining a higher pH at which the loss of ammonia is appreciable.

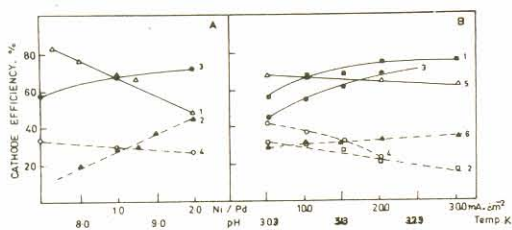


Fig. 1: Effect of operating conditions on the partial cathode efficiencies of nickel and palladium.

A: 1 & 2 Effect of Ni/Pd ratio at pH 8.5
3 & 4 Effect of pH at Ni/Pd : 1.25
1 & 3 Palladium; 2 & 4 Nickel
Electrolyte : NH_4Cl 0.2M, 10 mA.cm^{-2}

B: 1 - 4 Effect of current density (1 & 2 unstirred; 3 & 4 stirred)
5 & 6 Effect of temperature
1, 3 & 5 Palladium; 2, 4 & 6 Nickel
Electrolyte as in A

The Hull cell patterns (Fig. 2) indicate that increasing nickel content helps in producing good, adherent deposits even at low current densities. Deposits corresponding to current densities of 20, 15 and 10 mA.cm^{-2} at pH 9.5, 8.5 and 7.5 respectively

are exfoliated, presumably due to high stress. A higher electrolyte temperature is found to extend the permissible current density range of obtaining adherent deposits which, however, become gray black above 318 K.

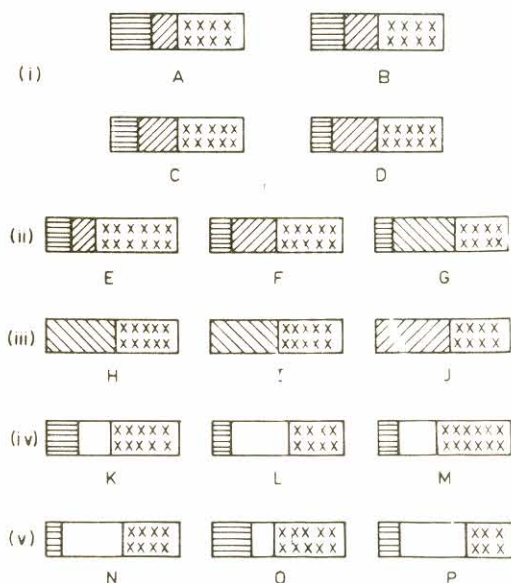


Fig. 2: Hull cell patterns for Ni-Pd alloy deposition: Code: \diagup Matt; \times Semi-bright; \equiv Hazy; \parallel Stressed; \square Bright

- (i) Effect of nickel concentration: Pd: 0.2M; NH_4Cl : 0.2M pH : 8.5, 303K, 1A, 5 min.; Ni/Pd(M): A, 0.5; B, 1.0; C, 1.25; D, 1.5
- (ii) Effect of pH: Pd: 0.2M, Ni:0.25M, others as above pH: E: 7.5; F: 8.5; G: 9.5;
- (iii) Effect of temperature: Conditions as in (ii) Temp: H: 303K; I: 313K; J: 323K
- (iv) Effect of additives: Conditions as above. Saccharin(gpl): K: 1.0; L: 2.0; M: 4.0
- (v) Saccharin 2.0 gpl with diol(gpl): N: 0.1; O: 0.2; P: 0.2 with NSA 1.0 gpl

Saccharin at a concentration of 1.0 g.l^{-1} as an additive has very little influence on the nature of the alloy deposits. When however, its concentration is above 2.0 g.l^{-1} , not only an improvement in the appearance of the pattern, but also absence of any exfoliation became evident. Addition of 0.005 to 0.1 g.l^{-1} butyne diol gives rise to bright deposits in presence of saccharin. However, a higher butyne diol concentration results in deterioration of the quality of Hull cell pattern. Presence of 1 g.l^{-1} α -naphthalene sulphonic acid in solution leads to improvement of the pattern apart from improving current density range.

As indicated in Fig. 3, the throwing power of the electrolyte increases with increasing (1) nickel content (2) current density (upto 20 mA.cm^{-2}) and (3) pH, but decreases with temperature. The higher throwing power of the alloy plating electrolyte compared to palladium electrolyte can be attributed to the higher polarisation associated with the deposition of the alloy.

The deposits produced in the absence of additives have a bright appearance only upto a thickness of $5 \mu\text{m}$. The bright deposits, however, have a higher level of brightness reaching 95% in the thickness range of 5-

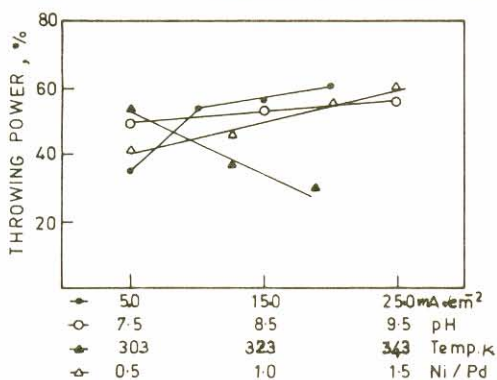


Fig. 3: Variation of throwing power of the electrolyte with operating conditions. Conditions: Ni/Pd: 1:25; NH_4Cl : 0.2M; pH: 8.5; 10 mA.cm^{-2} ; 303K unless otherwise specified.

$10 \mu\text{m}$. The extent of levelling of $5 \mu\text{m}$ thick deposits increased from 6% to 35% by the use of brighteners (Fig. 4).

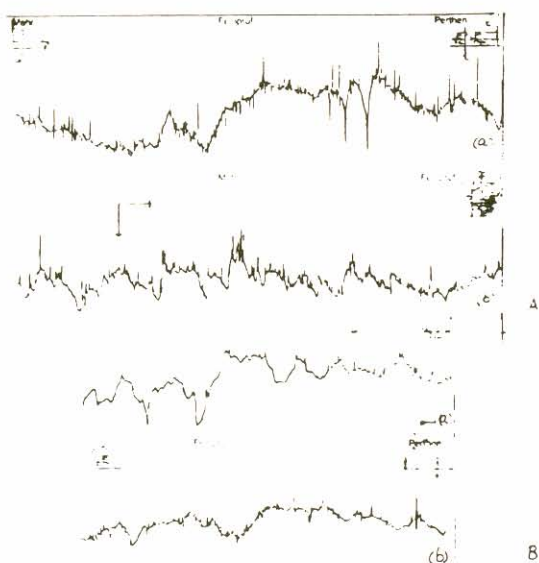


Fig. 4: Levelling measurements using Perthometer

A: Matt Pd. - 20% Ni alloy. Conditions: Deposit thickness $5 \mu\text{m}$; Vertical: $1 \mu\text{m}$; Horizontal: $250 \mu\text{m}$. (a) Surface profile before deposition, R_a : $0.6 \mu\text{m}$; (b) Surface profile after deposition, R_a : $0.56 \mu\text{m}$.

B: Bright Pd-20% Ni alloy, Conditions as above. (a) Initial R_a : $0.58 \mu\text{m}$; (b) Final, R_a : $0.38 \mu\text{m}$; % levelling: 34.5

Pure palladium deposits have a high hydrogen content. The outgassing of large amounts of hydrogen trapped in the crystalline lattice during electrodeposition causes poor deposit adhesion and results in cracking and flaking of the deposits. The hydrogen permeation current (Tables II and III and Fig. 5) decreases with increasing nickel content of the alloy and the J_r value is less for the alloy containing 20-27% nickel. The maximum and residual permeation currents are very high at low current densities (5.0 mA.cm^{-2}). Though J_m is low at 30 mA.cm^{-2} , J_r increases probably due to the high stress and cracked nature of the coating. The results also indicate the pH values of less than 7.5 and higher than 9.5 are not suitable for alloy deposition as they increase the hydrogen content. Saccharin helps in reducing the hydrogen content but butyne diol increases

it considerably. Hence adequate caution should be exercised in controlling the additive concentration.

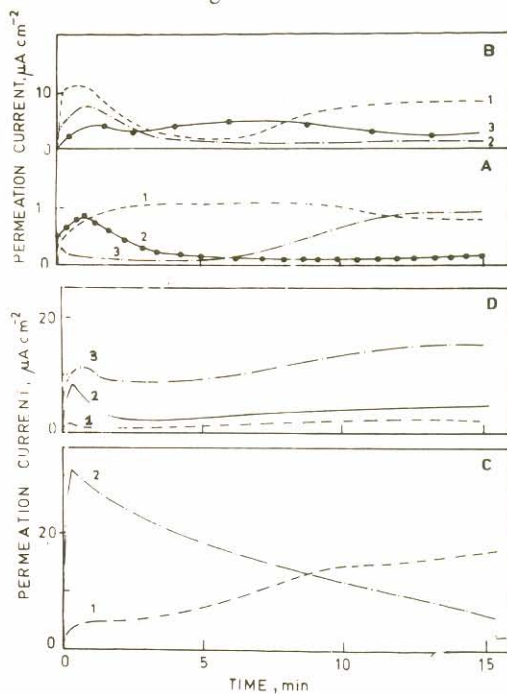


Fig. 5: Hydrogen permeation in Pd-Ni alloy deposition. Conditions as in Fig. 4 unless otherwise stated. (A) Effect of Ni/Pd ratio. (1) 0.5 (2) 1.0 (3) 2.0. (B) Effect of current density: (mA.cm^{-2}) (1) 5 (2) 15 (3) 30. (C) Effect of pH. (1) 7.5 (2) 9.5. (D) Effect of additives: (1)-Electrolyte with 2.0 g.l^{-1} saccharin (2) Saccharin 2.0 g.l^{-1} with diol 0.1 g.l^{-1} (3) Saccharin 2.0 g.l^{-1} with diol 0.2 g.l^{-1}

TABLE-II: Hydrogen permeation characteristics of nickel-palladium alloy deposition

Ni content of deposit %	Maximum permeation current J_m (μA)	Residual permeation current J_r (μA)	Quantity of adsorbed hydrogen QH ($\text{g atom.cm}^{-2} \times 10^{-8}$)
12.5	10.0	10.0	5.8
20.0	8.0	1.5	1.92
27.0	2.0	1.5	1.02
Bright 20% alloy*	1.5	1.5	0.902

* In presence of 2.0 g.l^{-1} saccharin, 0.05 g.l^{-1} diol and 1.0 g.l^{-1} NSA

CONCLUSION

With an ammine chloride electrolyte, good palladium-nickel alloy deposits containing 18 - 25% nickel can be obtained in the current density range of $10 - 20 \text{ mA.cm}^{-2}$, at pH 8.5 and at room temperature.

REFERENCES

1. I R A Christie, *Trans Inst Metal Finish*, 60 (1982) 33
2. K J Whitelaw, *ibid*, 60 (1982) 141

TABLE-III: Hydrogen permeation characteristics of nickel-palladium alloy deposition at different current densities and pH values

Ni 0.25M, Pd 0.2M, NH ₄ Cl 0.2M, pH 8.5, 303K		Maximum permeation current J _m (μA)	Residual permeation J _r (μA)	Quantity of hydrogen adsorbed QH (g atom.cm ⁻² × 10 ⁻⁸)
C.d. (mA.cm ⁻²)	pH			
5	8.5	10.0	8.0	3.05
15	8.5	8.0	1.5	1.92
30	8.5	5.0	5.0	3.01
15	7.5	5.0	15.0	4.81
15	9.5	31.0	12.0	6.64

3. B O Hara, *ibid*, 60 (1982) 156
4. J S Stevenson, *ibid*, 59 (1981) 113
5. *Platinum Metals Review*, 29-2 (1984) 61
6. G Brauer, *Handbook of Preparative Inorganic Chemistry*, Vol. II, Academic Press, New York (1960)
7. A Brenner, *Electrodeposition of Alloys - Principles and Practices*, Vol. 1 and 2, Academic Press, New York (1963)
8. F A Lowenheim, *Modern Electroplating*, John Wiley & Sons, New York (1980)
9. M A Devanathan and Z Stachurski, *Proc Roy Soc, London*, A 270 (1962) 90
10. N V Parthasaradhy, Ph.D. Thesis, Banaras Hindu University (1971)
11. Y Fukumoto, Y Kawashima and T Hayashi, *Surf Coat Technol*, 27- 2 (1986) 145
12. Ch J Raub, *Proc AES Symp Economic Use of and Substitution for Precious Metals*, Sept 16 (1980)